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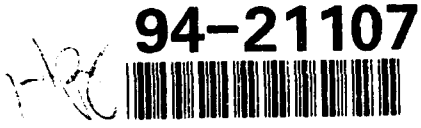

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FINAL REPORT

RESEARCH INVESTIGATION DIRECTED TOWARD EXTENDING THE USEFUL RANGE OF THE ELECTROMAGNETIC SPECTRUM

Contract DAAL03-91-C-0016
For the Period April 1, 1991 - March 31, 1994

Presented to:

THE JOINT SERVICES TECHNICAL ADVISORY COMMITTEE
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THE OFFICE OF NAVAL RESEARCH,
and THE AIR FORCE OFFICE OF SCIENTIFIC RESEARCH

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COLUMBIA RADIATION LABORATORY

JSEP FINAL REPORT

Contract DAAL03-91-C-0016
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Contents

I. PRINCIPAL INVESTIGATORS:

Dr. Brian E. Bent
Dr. George W. Flynn
Dr. Irving P. Herman
Dr. Richard M. Osgood, Jr.
Dr. Malvin C. Teich
Dr. Robert C. White
Dr. Edward S. Yang

II. SUMMARY OF RESEARCH ACCOMPLISHMENTS

NONCLASSICAL LIGHT GENERATION AND DETECTION (M. C. Teich, Principal Investigator)

We have used fractal shot noise as the rate of a doubly stochastic Poisson point process (DSPP); the resulting process exhibits a power spectral density with $1/f$-type behavior and a non-Gaussian amplitude probability density function. It has many applications including charge transport in amorphous semiconductors. We have also determined the behavior of the fractal renewal point process. We have studied the effects of tensile strain on exciton absorption in compound semiconductor devices and the relative merits of quantum-wire and quantum-well long-wavelength semiconductor lasers. We have determined the conditions under which the channel capacity of an optical receiver can be improved by modifying an initially Poisson photon stream and making it sub-Poisson. We have obtained a closed-form solution for the photon-counting distribution at the output of a cascade of optical (e.g., erbium-doped fiber-optic) amplifiers. We have conducted experiments in which entangled photon pairs generated by parametric downconversion have been interfered with each other in a Mach-Zehnder interferometer.

NEW OPTICAL MATERIALS AND SOURCES (I. P. Herman, Principal Investigator)

Over the last three years, Professor Herman's group investigated the importance of strain and confinement in determining the optical properties of semiconductor heterostructures. The focus of these studies was novel materials that are potentially useful as active regions in light-emitting devices. Biaxial strain has been tuned in semiconductor heterostructures by applying hydrostatic pressure. This has been observed by photoluminescence (ZeSe epilayers on GaAs) and by Raman scattering of phonons (Ge/Si superlattices). Pressure studies also showed that ZnMnSe/ZnSe superlattices have type I band alignment. Raman scattering was used to understand the confinement of phonons, and therefore the structure, of light-emitting porous silicon. GeSi alloys were probed by Raman scattering at high temperatures, which is useful for in situ thermometry, and at high pressures, which is useful for characterizing strain in these materials. Models were also developed to explain how pressure can be used to tune biaxial strain in arbitrary semiconductor heterostructures, and how phonon dispersion in Si and Ge is affected by arbitrary strain. A modified Keating/valence force field model was developed for the latter model.

Professor Herman also began a new collaboration with Professor Osgood which is described below.

ULTRAVIOLET TWO-PHOTON LASER PHOTOELECTRON STUDIES OF EXCITED SEMICONDUCTOR SURFACES (R. M. Osgood, Jr., Principal Investigator)

During this three year period, Professor Osgood's effort has focused on developing new experimental techniques for expanding the measurements of interfacial electronic structure to unoccupied bands--that is those collaborative projects within the Columbia JSEP community. Specifically, with regard to the first project, he has shown that two-photon photoemission can be used to probe very short-lived states on single-crystal transition-metal surfaces. Using this material system the group has selected one particular electronic system, that of image electrons, as a model system for developing this excited-state probing technique and for showing that these simple electronic systems can be used as an effective probe of surface conditions. With regard to collaborative interactions, Professor Osgood has developed a joint project with Professor Herman to use photoluminescence to probe the surface properties of etched nanostructures. This is a research direction which is currently of much importance for the national nanoscale electronics program and yet, surprisingly, nanoscale surface science is a relatively unexplored area at present. In addition, Professor Osgood has begun a collaborative program with Professor Teich to develop integrated forms of his correlated photon-pair optical devices.

INVESTIGATION AND CONTROL OF COLLISION PROCESSES FOR QUANTUM ELECTRONICS AND MICROELECTRONICS (G. W. Flynn, Principal Investigator)

The overall objective of our work evolved significantly during the past three years. Our initial efforts were focused on attempts to understand the fundamental physical and chemical processes which determine the exchange of energy during collisions between molecules, atoms, and electrons, and to use this information to control the rates of gas-surface reactions or the production of specific quantum states of molecules. The control of gas-surface chemical reaction rates is, of course, critical in the development of improved microelectronic devices, while a knowledge of the factors which determine the quantum states resulting from a collision process is crucial in the development of more efficient and novel laser devices. The study of electron-molecule collisions is directly related to the processes which occur in plasma etching reactors and which control the identity and physical characteristics of the chemically reactive species that are responsible for the etching of microchips. In addition these same interactions are of considerable importance in the gas laser field where electron-atom or electron-molecule collisions provide one of the major methods for producing metastable species necessary for laser action.

Our work on electron-molecule collision processes led in an intellectually natural way to the study of electron tunneling processes. We have pursued these via an experimental program in scanning tunneling microscopy (STM), which has been aimed at the study of molecules adsorbed on surfaces. This STM work has already been successful in identifying a number of important structural and dynamical issues for several surface-adsorbate systems. These studies are of importance in the development of the next generation of electronic and opto-electronic devices, which will require molecular films with very specific mechanical and electronic properties. Advances in organic synthetic methods as well as in assembly techniques are making feasible the production of films with specific electronic and chemical properties. Non-destructive probes are also required to investigate such films and to establish the relationship between structure at the atomic or molecular level and the function of these films at the macroscopic level. These structure-function relationships are certain to play a major role in the development of thin polymer films for use in microelectronics packaging applications. The scanning tunneling microscope is nearly an ideal device to use in the elucidation of these relationships since it has proven to be a remarkable tool for studying surface features and surface electronic structure as well as changes in these features due to chemical reactions.

Our objectives have been to use the STM to study the structure and properties of a number of thin polymer films, molecular adsorbates, and self-assembled monolayers. These efforts are focused on investigations of surface adsorbate interactions, the nature of the STM contrast mechanism for molecules adsorbed on surfaces, the effect of the chemical nature of liquid solvents on the geometric packing of adsorbates and their bonding to surfaces, and the role played by the underlying structure of the surface itself (defects, domains, etc.) in determining the arrangement of these molecular adsorbates. Information concerning adsorbate molecule structures at the solid/liquid interface is relevant for a number of macroscopic scale surface phenomena such as lubrication and adhesion. On the atomic scale issues such as the underlying substrate structure and its effect on the orientation of surface adsorbates are critical in developing electronic devices based on liquid crystal molecules and chemically functionalized surfaces which rely on molecular recognition for chemical sensors and chromatography. In addition, studies of molecular monolayers and their two-dimensional structures are of theoretical interest because true crystalline order at finite temperatures is not possible in a two-dimensional system. A considerable amount of data obtained from both classical thermochemistry experiments and more modern surface analytical techniques is available in the literature which provides information complementary to that obtained from STM images.

In the future we plan to pursue UHV STM experiments designed to investigate surface reconstructions brought about by all chemical "digital etching" and chemical reactions of surface adsorbates. All of these experiments are aimed at the elucidation and control of surface and adsorbate structures and their relationship to the electronic and chemical properties of materials.

INTERFACE STUDIES AND DEVICE APPLICATIONS OF MULTI-LAYERED SCHOTTKY BARRIER AND HETEROJUNCTION STRUCTURES (E. S. Yang, Principal Investigator)

In the last three years, we have focused our studies on the chemical and electrical properties of interfaces involving $Si_{1-x}Ge_x$ alloys. For $x < 0.5$, Schottky barriers can be formed with Pd and Pt but the barrier height depends on Ge segregation. We have developed a novel method of forming a nonalloyed ohmic contact on n-Si using a strained $Si_{0.5}Ge_{0.5}$ buffer layer. Along with a tungsten diffusion barrier, stable ohmic contacts were maintained up to 550°C for 30 minutes.

We have employed an electron cyclotron resonance (ECR) microwave plasma to produce a high-quality silicon-germanium oxide on a $Si_{1-x}Ge_x$ epitaxial layer. Both MBE and UHV/CVD epilayers were studied and the UHV/CVD materials were found to be superior with an interface states density a factor of 2 to 5 below that of the MBE samples. So far, the best interface states density is around 10^{11} $cm^{-2} \circ eV^{-1}$ for aluminum-gate MOS capacitors. The oxide was found to be stoichiometric from x-ray photoelectron spectroscopy (XPS) studies. Low field surface hole mobility is found to be 167 $cm^2/V\text{-}s$ at 300 K and 530 $cm^2/V\text{-}s$ at 77 K. The corresponding hole mobilities for Si are 140 $cm^2/V\text{-}s$ at 300 K and 420 $cm^2/V\text{-}s$ at 77 K.

In addition to the ECR oxidation of SiGe, we have also discovered a process of passivating GaAs surface by ECR hydrogen cleaning and ammonia plasmas forming of a thin surface nitride. Exposed junction leakage current is found to be reduced by a factor of 200 after ECR passivation giving rise to a corresponding increase in the current gain of a heterojunction bipolar transistor.

SURFACE SCIENCE STUDIES OF POLYMER THIN FILMS FOR ADVANCED INTERCONNECT AND PACKAGING TECHNOLOGY
(B. E. Bent and R. C. White, Principal Investigators)

Research over the past three years has focused on new methods for depositing and characterizing polymer thin films to develop molecular-scale control of packaging processes. In the area of polymer film deposition, ultra-thin films (50 - 100 Å) have been prepared by spin-coating aluminum- and gold-coated silicon substrates, and these films have been characterized by scanning tunneling microscopy (STM), x-ray photoelectron spectroscopy (XPS), and Fourier transform infrared spectroscopy (FTIR). The STM results indicate a dramatic variation in the topographic and electronic properties of these films at the molecular level when these films are exposed to water vapor, while the vibrational spectra indicate preferential ordering of the polymer backbone at the substrate/film interface.

The use of molecular self-assembly to prepare single monolayer organic films has also been explored, and a number of techniques for adding or removing atoms from adsorbed molecules to form these monolayers have been demonstrated. Vibrational spectra of these monolayers indicate that the adsorbed molecules are oriented with the hydrocarbon chains pointing away from the surface, and it has been shown that the thermal stability of films on copper surfaces is limited by a facile hydrogen abstraction reaction by the metal substrate. This reaction depends on the presence of unoccupied sites in the monolayer, and by blocking these sites with iodine atoms, a small fraction of the monolayer can be stabilized by orders of magnitude.

In the area of atomic control of surface processing, which is a recently-initiated effort, the mechanisms by which H atoms react with and remove organic monolayers from copper surfaces have been studied. The results show that chemical reactions in these systems occur at temperatures as low as 110 K as a result of a novel mechanism in which the H atoms react directly with the hydrocarbons without first bonding (and thermally-accommodating) to the metal surface. The chemical dry etching of GaAs surfaces was also investigated using halogen-containing molecules, and evidence was obtained for selective removal of Ga from the surface at 600 - 670 K when HCl is the etchant. These results have initiated studies of possible procedures for digital etching of GaAs.

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S. Zolgharnain and R. C. White, "In-vacuum Synthesis and Characterization of Thin Aromatic Polyimide Films Prepared by a Chemical Vapor Deposition Process," submitted to J. Vac. Sci. Technol.

R. C. White, Electrical Properties of Microelectronics Packaging Materials," invited review chapter, in *Behavior of Materials in Microelectronics and Fiber-Optic Systems,* E. Suhir, Ed., Oxford University Press, in preparation.

E. N. Schulman and R. C. White, "Giant Conductance Fluctuations in Ultrasmall-Area Tunnel Junctions of a Poor Organic Conductor." submitted, Physical Review Letters.

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IV. LIST OF JSEP SUPPORTED GRADUATES, April 1, 1991 - March 31, 1994

Bulovic, V., M.S.
Campos, R. A., Ph.D.
Chiang, C.-M., Ph.D.
Chou, J., Ph.D.
Jenks, C., Ph.D.
Jeong, H. S., Ph.D.
Jiang, J. C., Ph.D.
Jiang, Y.-J., Ph.D.
Larchuk, T. S., Ph.D.
Leang, P., Ph.D.
Lee, Y. S., Ph.D.
Li, P.-W., Ph.D.
Li, T., Ph.D.
Lin, J.-L., Ph.D.
Liou, H.-K., Ph.D.
Liu, H., B. S.
Lowen, S. B., Ph.D. (JSEP Fellow)
Lu, Z., Ph.D.
Melnikov, K., M.S.
New, J., B. S.
Ni, K., Ph.D.
Paiella, R., M. S.
Paul, A., Ph.D.
Quiniou, B., Ph.D.
Saban, D., B. S.
Singer, F., Ph.D.
Su, C., Ph.D.
Sui, Z., Ph.D.
Tolman, S., B. S.
Tuchman, J., Ph.D.
Wang, Q., Ph.D.
Xi, M., Ph.D.
Zheng, L., Ph.D.
Zhu, L., Ph.D.
Zhu, N., Ph.D.
Zolgharnain, S., M.S.